THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

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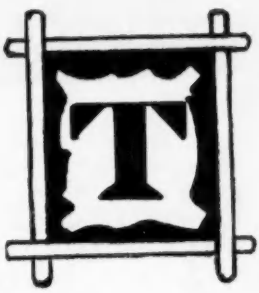

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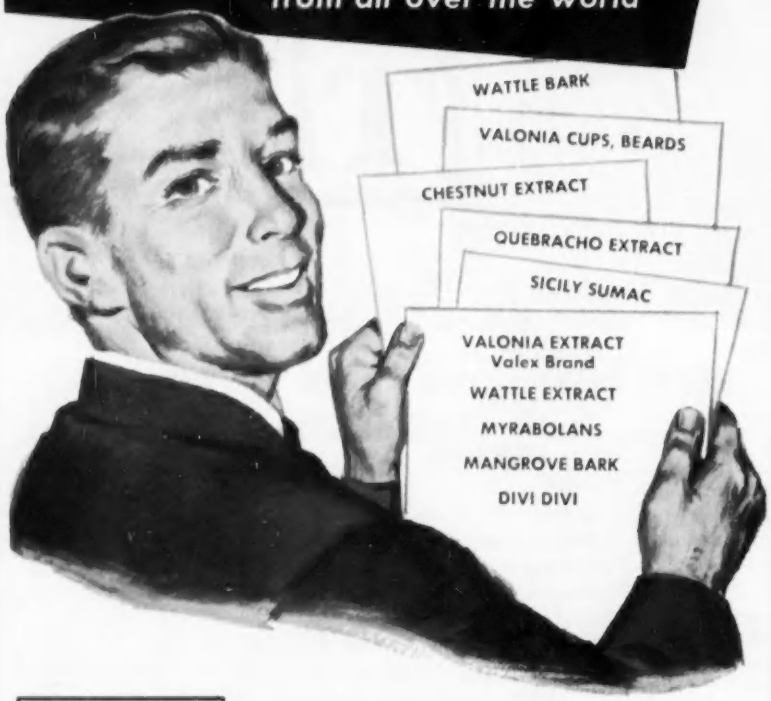

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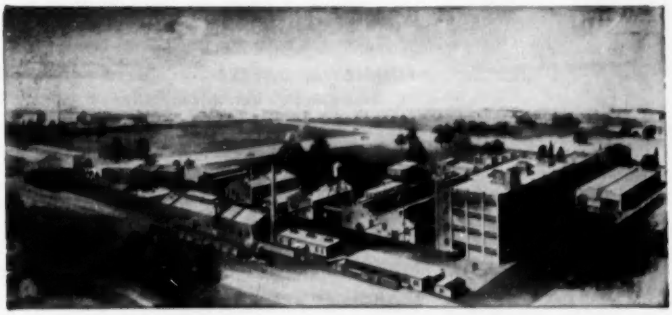

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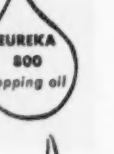
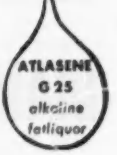


How many of those names do you recognize as "old friends?" How many of the new ones are you familiar with?



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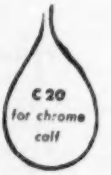

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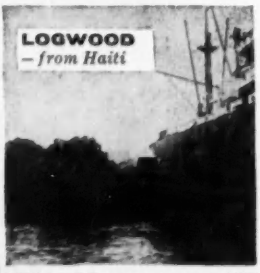

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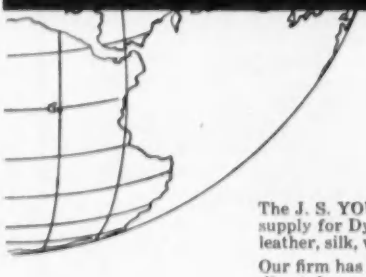

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Vol. LI JANUARY 1956 No. 1

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CONVENTION NOTICE

The 1956 annual meeting will be held at the Grand Hotel, Mackinac Island, Michigan on June 17-18-19-20.

All persons desiring to present papers are requested to submit a brief abstract of the paper to:

Mr. Harold R. Miller, Chairman
Convention Committee
c/o A. F. Gallun & Sons Corp.
1818 North Water Street
Milwaukee 1, Wisconsin

All abstracts must be in our hands by February 29, 1956.

H. R. MILLER, *Chairman*
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MUTUAL MEMBER HONORED

DR. K. H. GUSTAVSON

The Royal Swedish Academy of Technical Sciences (IVA), has conferred its highest mark of distinction, the IVA Grand Gold Medal, on Dr. K. H. Gustavson, the Swedish Tanning Research Institute, Stockholm, in recognition of his pioneering contributions to the chemistry and reactivity of collagen, and for his investigations of the mechanism of tannage, particularly his research on the reaction of chromium compounds with hide protein in chrome tanning.

BUSINESS MEETING OF A.L.C.A.

(Held during the 1955 Annual Meeting at Swampscott, Mass.)

PRESIDENT FLINN: Our by-laws insist that we hold a business meeting each year. This year, we have two items of business for comment from our organization, unless there are others from the floor.

The first can be dismissed in passing. This deals with the provisonal methods as they are now written. Strictly, according to our by-laws, we should take vote on these since they are now one year old. Unfortunately the full complement of the methods is not yet published, and until they are, we shall withhold voting on these methods until next year.

The second item of business is a discussion of a joint committee to work with the ASTM in the development of methods of analysis for leather to be used by the ASTM. I would like Dr. O'Flaherty to explain this.

DR. O'FLAHERTY: The ASTM, for the benefit of those who may not know, is the American Society for Testing Materials. They met in Cincinnati—it is an international society—some several months ago.

At that time one of their representatives came to see me and said, "Why is it that the leather interests do not have some association with us?" I referred the matter to the Council and at their meeting in February a Committee, headed by Mr. Maeser as Chairman, was asked to look into the matter and get the full details.

Mr. Maeser has had considerable correspondence with the people at ASTM and subsequently he, and Mr. Thorstensen, met with representatives of the ASTM in Philadelphia, and went over the matter, spending many hours getting the full details.

In the main it amounts to this: ASTM would be willing to accept in toto our present methods. I am speaking more especially about physical test methods. And then they would create a committee and that committee would be made up in the main of leather interests, of allied interests, of manufacturers of leather interests, and of consumer interests in leather—a committee, they visualize, of about thirty persons. Probably that is their minimum.

Since our methods would be accepted in toto, they would remain so until such time as they were found inadequate or insufficient, and at that time they would then be referred to the committee.

Last night when Council met, they thought it was a very good idea and approved it in principle. No final details, however, have been established. Yet it was Council's wish to bring this before the membership because it is their particular tool, if you like. And therefore I am sure our President will ask you to voice your opinion on it.

One or two items may come to your mind and I shall try to anticipate them and answer them quickly.

How much does it cost? Nominal. One or two members of our Society may also be members of ASTM and that would suffice.

If there are new methods or methods to be revised, we feel that ASTM would be insistent that sufficient amount of research be accomplished before they be accepted. Council felt it might be very smart to start with the Physical Test methods and, if it works out, then we can consider doing it for the Chemical methods. If it does not work out, then it could be dropped at that time.

I hope I have covered it rather quickly and given you a full picture. If anyone should have any specific questions, I am sure that Mr. Maeser or Mr. Thorstensen could answer them in detail.

PRESIDENT FLINN: Dr. Turley?

DR. TURLEY: Can you tell us what would be the proportionate representation of the ALCA on thse ASTM committees that would deal specifically with any questions that arise with leather? Are we going to be strongly represented, or will we be in the minority?

DR. O'FLAHERTY: Last evening when we spoke about it, the thought was that perhaps we should have about five members out of the thirty. However, it does not mean there is an antagonistic effort. The consumers of leather, shoe manufacturers perhaps, being a big entity, and consumers of leather, would also be represented, to get their viewpoints more especially.

MR. MAESER: Dr. Turley, I cannot answer that specifically at the present time for though I have had some years of personal experience with ASTM committees, I have forgotten their exact committee organization. I do not have the ASTM requirements with me or I could read them to you. They insist that manufacturers of the product be represented and that users of the product be represented. And in almost all cases they attempt to have representatives of the Government Bureaus on the committee.

I would think that the most important point is that the whole effort would be a joint effort between the two Associations. We are not going to be absorbed by the ASTM at all. The whole thing will be done under the auspices of the two Associations equally sponsored and handled, and such methods as are developed would be published as joint methods of the two Associations. That has been understood quite clearly in all our dealings to date.

DR. HOBBS: Perhaps I could add a bit to what Slim has said, having been a member of both ALCA and ASTM for a number of years. The representation on the ASTM committee is supposed to be divided among producers, consumers, and general interests. ALCA would not be represented as ALCA members or delegates, but indirectly to the extent that some of these producer members, some of the consumer members, and some of the general interest members would also happen to be ALCA members.

Similiarly, they do not have representatives of the Federal Government as such, but because the Government is interested in these various materials, from a general interest point of view and to some extent as a consumer, and also because of the Government's interest in setting up standard methods and procedures, some Government men will be found on ASTM committees.

ASTM does like to make sure that no one of these three groups is a majority on any one committee. So that leather manufacturers would not be more than half, nor would consumers.

I think the particular advantage of such a tie-up that might accrue to us would be that we would get the point of view and the experiences of consumers—some consumers particularly—who use leather to a small extent

but not enough to make them feel justified in taking full membership in ALCA and working on that.

For instance, in the field of paper, we have representatives from outfits like Ford Motor Company and General Electric, who use it to some extent, but are not primarily paper technologists. Yet they can bring considerable help to us in setting up standard methods. That is one of the principal advantages that we would gain—in adding to the total of experience that goes into these methods.

DR. R. M. KOPPENHOEFER (Socony-Mobil Oil Company): For the past five years, I have been Vice Chairman of a joint ASTM and TAPPI Committee on wax testing and what Bob Hobbs says is true. The ASTM does definitely outline the character of the committee and prevents you from having a preponderance of either consumer or producers groups. However, as I recollect, the methods are published by both Associations.

For instance, when we finish a method, it goes to ASTM for their approval and we must comply with their requirements and we must also comply with TAPPI'S requirements and oftentimes there is a little tightrope walking to be done. Sometimes the method is written up in different detail to satisfy both organizations.

Where there is cross-interest such as here, where ASTM was working on wax and the paper industry was working also on wax, the advantage of a joint committee so that we would not come up with two procedures, was an obvious advantage. Where we have that situation, we should certainly do cooperative work.

PRESIDENT FLINN: Our own official methods would be those of the Association and would not be altered. As Dr. Hobbs has implied, certain benefits accrue by having these methods joint methods with the ASTM. These would be joint methods and published as such.

At the present time, I am sure you are all aware that there are no methods for leather analysis, either physical or chemical, in the ASTM Manuals. It was the consensus of Council that we should proceed on this tentative basis with the physical testing methods and if all went well, we would consider the chemical testing methods.

We will accept further discussion but in due course we would like to get the consensus regarding your own belief. Is there more discussion at this time?

DR. GEORGE H. VON FUCHS (Consultant): I have been a member of ASTM for seventeen years and have repeatedly asked the ASTM management why it did not have a leather committee, particularly since I became interested in leather.

I can warmly recommend your joining this organization. It will have the

advantage of a much larger, nationwide and internationally organized group who have been in business for a long time and they will give you publicity, will make our test methods available to the whole world. So I am in favor of it. I am Chairman of one ASTM Section and Secretary of another and find this work exteremely interesting, and useful.

PRESIDENT FLINN: Is there further comment? If not, I would appreciate a showing of hands as to whether we should continue along this line of thinking and start this tentative arrangement on the physical testing methods. All those in favor, please raise your hands. (You must be a member of our Association to vote.)

DR. O'FLAHERTY: The large majority voted yes.

PRESIDENT FLINN: Those who are opposed? (About two or three).

PRESIDENT FLINN: It is approved and is so ordered. We shall proceed as you have indicated.

If there is no further business from the floor, we will stand adjourned.

(The session adjourned at 4:30 p.m.)

Polymerization of Resins In Relation To Leather Finishes*

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ABSTRACT

The use of resin emulsion in leather finishes has become standard industry practice in the past decade.

A discussion of the problems of polymerizing these emulsions will be presented indicating the multitude of variations in film character, gloss, mechanical stability and adhesion that can be obtained by varying emulsifier type and content, monomer composition, particle size, initiator system, etc. The roles of compounding vs. polymerization in formulating suitable leather finishes will be compared.

In general, the proper choice of a polymer emulsion permits the solution of many more difficult finishing problems than does the compounding of an otherwise unsatisfactory emulsion.

Water finishes for leather are very complex organic-inorganic systems comprising mixtures of natural and synthetic waxes, gums, proteins, pigments, dyes, alkalies, preservatives, leveling agents, and synthetic resin emulsions.

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The scientific compounding of these ingredients has resulted in the high quality finishes being manufactured today.

The "infant" of the finish manufacturers' raw material supply is the broad group of products known as synthetic resin emulsions. It is these emulsions, whose use has grown tremendously in the past several decades, which will be the major aspect of the present discussion. These products have received overwhelming acceptance since they have permitted the formulation of high quality finishes for all types of leather with enhanced appearance and utility.

The increased trend towards the use of resin emulsions made it appear valuable to discuss the fundamentals of their preparation, and the variations which can be achieved in hardness, gloss, feel, flexibility, etc. Information of this type should be of interest to all those concerned with the use of these materials and, it is hoped, will permit closer liason between those who manufacture and those who use synthetic resin emulsions in the leather industry. The resin emulsion types of the future, and their quality, will depend upon how well the user and manufacturer communicate with one another.

Many books and reviews have been written on the subject of polymerization [1, 2, 3, 4], and it is the intent of the authors of this paper to relate this information to the particular requirements of the leather industry.

A. Polymerization

Prior to a discussion of the wide variety of resin emulsions which are presently or potentially available, it is desirable to describe, in a brief way, the fundamentals of polymerization, i. e., what polymers are and how polymers are prepared, controlled and modified. It also affords the opportunity to illustrate the complexity and sensitivity of emulsion polymerizations.

Basically, polymerization involves the conversion of a low molecular weight substance, the monomer, into a high molecular weight substance, the polymer. Monomers consist of relatively simple chemical molecules with one or more reactive double bonds, such as: acrylic esters, styrene, acrylonitrile, vinyl acetate, butadiene, etc. Polymers consist of long chains of chemically combined monomers, i. e., 100 to 10,000 monomer units per polymer chain. The chain may consist of only one monomer type (homopolymer) or of several monomers (copolymer).

The polymerization reaction mechanism involves four basic steps, indicated below:

1. *Initiation*: The formation of an "activated" molecule (free radical) by the decomposition of an initiator, (peroxide, persulphate, etc.,) to form the first link in the polymer chain.

$$H_2O_2 \rightarrow 2OH^*$$

The asterisk(*) denotes a free radical.

2. *Propagation*: The successive rapid addition of monomer units to the initiator radical to form a long polymer chain, still activated.

$$HO^{*} + \underset{R}{CH}=CH_2 \rightarrow HO\underset{R}{CH}-CH_2^{*}$$

$$HO\underset{R}{CH}-CH_2^{*} + \times \underset{R}{CH}=CH_2 \rightarrow HO\left(\underset{R}{CH}-CH_2\right)_{\times}\underset{R}{CH}-CH_2^{*}$$

3. *Termination*: The cessation of polymer chain growth by the reaction of two radicals to form a stable polymer.

$$HO\left(\underset{R}{CH}-CH_2\right)_{X}\underset{R}{CH}-CH_2^{*} + HO^{*} \rightarrow HO\left(\underset{R}{CH}-CH_2\right)_{X}\underset{R}{CH}-CH_2OH$$

4. *Chain Transfer*: The reaction of an active chain radical with another substance resulting in the termination of the chain while transferring the radical character to the other substance.

$$HO\left(\underset{R}{CH}-CH_2\right)_{X}\underset{R}{CH}-CH_2^{*} + RSH \rightarrow HO\left(\underset{R}{CH}-CH_2\right)_{X}\underset{R}{CH}-CH_2H + RS^{*}$$

The chain transfer reaction results in a lower molecular weight polymer without affecting the rate of polymerization. Certain materials are particularly effective chain transfer agents and are utilized in polymerization technology to control the molecular weight to the specifications of the consuming industry. These include mercaptans, chlorinated hydrocarbons, and aldehydes.

The first three steps, illustrated above, occur for each of the millions of polymer molecules formed in any polymerization reaction, whether carried out by bulk or suspension polymerization, solution polymerization or emulsion polymerization. The chain transfer reaction occurs with varying frequency depending upon the particular system.

It should also be noted that the sequence of steps to form any polymer molecule occurs in a fraction of a second. All the molecules do not polymerize at the same time so the overall polymerization may take many hours.

B. Emulsion Polymerization

This polymerization method is the most important for the leather finish industry and the balance of the paper will be devoted to this subject.

The emulsion method offers a number of advantages:

(1) The product is obtained directly in the form in which it is to be used, i. e., as a finely divided solid polymer dispersed in water.

(2) The product is non-flammable.

(3) High solids may be obtained at low viscosities.

(4) The highest molecular weight polymers are obtained with increased strength, toughness, resilience, etc.

The emulsion method is also the most complex, requiring a carefully balanced selection of ingredients for optimum results. Typical ingredients are described below.

(a) *Water* is the diluent which forms the continuous phase for the oil-in-water emulsion in the early stages and the solid-in-water dispersion in the later stages. This usually constitutes 40 to 70 per cent of the total recipe. The *monomers* usually constitute 30 to 60 per cent of the total recipe.

(b) *Emulsifiers* are required to stabilize such systems, to prevent coagulation, creaming, etc. For emulsions designed for leather finishing, the primary emulsifiers are generally soaps or synthetic emulsifiers of the sulfate or sulfonate type. The latter materials, along with the nonionics, permit the preparation of polymer emulsions with optimum stability to pH changes and heavy metal ions which may be present in pigments, hard water, etc. The emulsifiers usually constitute 0.5 to 3 per cent of the total recipe.

(c) *Water soluble initiators*, such as hydrogen peroxide, potassium persulfate, etc., are required to initiate the polymerization reaction. (0.01 to 2 per cent of total recipe).

(d) *Accelerators* (trace metal salts), retarders (aromatic nitro compounds), and pH buffers are frequently employed to modify the reaction rate (0.01 to 0.5 per cent).

(e) *Protective Colloids* (natural gums, polyvinyl alcohol, cellulose derivatives, etc.) provide additional stability during manufacture and ultimate use and often are used in conjunction with emulsifiers. They also permit the direct manufacture of higher viscosity systems where desired. (0.1 to 5 per cent.).

(f) *Chain Transfer Agents* are often required for molecular weight control or to prevent objectionable side reactions, termed cross-linking, which impair desirable physical properties such as flexibility, abrasion resistance, etc. (0.01 to 1 per cent of charged monomer weight.)

(g) *Additional Ingredients* that are used in varying minor amounts include: sequestering agents, salts, solvents and plasticizers and polymerization "short-stops".

Thus the statement in an earlier section regarding the complexity of emulsion polymerization systems is borne out. The variations in monomers, initiators, emulsifiers, etc., that are available to the development chemist are innumerable and an extensive background in polymer chemistry, com-

bined with a thorough appreciation of the industry being served are prerequisites for the intelligent selection of these materials.

Emulsion polymerization also involves unique engineering consideration. The agitation system must not only be designed to cope with viscosities from less than that of water to heavy pastes. It must provide sufficient shear for good monomer emulsification and still avoid breakdown in mechanical stability of the polymer emulsion. It must not promote foaming or air entrapment. In addition to such mechanical specifications, the agitation intensity has considerable importance on the chemical behavior of the polymerization, affecting the induction time and also the molecular weight by influencing the rate of consumption of chain transfer agent. Paddles, turbines, propellers and scrapers may all be used depending on the type of polymerization and the polymerization technique.

Although the final polymer emulsion is non-flammable, and offers no hazard to the user, the polymer manufacturer must deal with flammable monomers. Furthermore, the polymerization reaction is strongly exothermic and heat removal must be effective to maintain the desired reaction temperature. Serious difficulties can occur if the reaction temperature cannot be controlled since any rise in temperature accelerates the reaction, further compounding the difficulties. Heat removal is accomplished by use of reflex condensers, jacket water circulation, semi-continuous or continuous operation, etc., and proper instrumentation is desirable to minimize and anticipate lags in the measuring or control system.

Careful engineering is also required to eliminate the introduction of any impurities or contaminants into the polymerization. Polymerizations are extremely sensitive to traces of impurities which may act as accelerators, inhibitors or modifiers. For example, minute quantities of certain metals, salts, amines, or quinones may have profound inhibiting effects and must be minimized by the use of suitable deionized water equipment.

C. Effect of Monomer Composition on Properties

All the ingredients in a polymerization recipe have an important bearing on the properties and ultimate application of the product.

The choice of monomers is particularly significant since it has the major influence on many of the desirable properties of the formulated leather finish. For example, plating, gloss, low temperature flexibility, crock resistance, leather "break" and "feel" may all be modified by suitable monomer choice.

A partial list of presently available monomers has been compiled as an example of the framework upon which the polymerization chemist builds. The list has been arranged in approximate order of increasing flexibility and softness.

TABLE I

Group A	Group B	Group C
Acrylonitrile	Vinyl Acetate	Longer chain methacrylates
Vinylidene Chloride	Isobutyl Methacrylate	Longer chain maleates and fumarates
Vinyl Chloride	Butyl Methacrylate	Longer chain vinyl esters and others
Styrene	Methyl Acrylate	Longer chain acrylates
Vinyl Toluene	Ethyl Acrylate	
Methyl Methacrylate	Vinyl-N-Butyl Ether	
	Butadiene	

Emulsion polymers prepared from Group A monomers yield powdery, discontinuous films when dried at room temperature and these homopolymers are generally unsuited for the formulation of leather finishes. Group B and C monomers yield polymers which deposit continuous films from emulsion which vary from hard, brittle materials to very soft and tacky materials. Many of the higher molecular weight Group C monomers yield waxy polymers since the long chain ends tend to crystallize much as do paraffin waxes. In those cases, the flexibility usually decreases.

All the monomers listed will undergo homopolymerization of the radical type readily except the maleates, fumarates and vinyl ethers. They are useful, nonetheless, because of the properties they impart when copolymerized with the other monomers.

It should be pointed out that not all these monomers will copolymerize with one another. Experience or reference to the literature are the only guides in such cases.

In observing the list above, it should be noted that flexibility generally increases with an increase in the length of the side chain. For example, flexibility increases in the methacrylate series as follows: methyl, ethyl, isobutyl, butyl. When extensive crystallization starts, i. e., stearyl methacrylate, the flexibility decreases again. Table I is useful as a general guide for the choice of suitable comonomers to achieve desired film characteristics. Although many copolymers will yield approximately the same film characteristics, the final choice will depend upon the auxiliary requirements of the end product.

For example, the following copolymer systems can be employed to yield approximately the same film properties by adjusting the monomer ratios:

1. Vinyl acetate-butyl acrylate
2. Styrene-butadiene
3. Acrylonitrile-butadiene
4. Methyl methacrylate-butyl acrylate

Copolymer (1) usually has the disadvantage of poor water resistance since vinyl acetate is inherently water sensitive. In addition, it has poor alkali

resistance. Copolymer (2) has poor adhesion to leather, to acrylic finishes and to most lacquers and also tends to discolor and embrittle with age. Copolymer (3) has excellent adhesion characteristics but is not as satisfactory as copolymer (4) for the formulation of white finishes since the butadiene tends to give poor light and heat resistance. Each of these properties could be predicted from the properties of the homopolymer and, it may be generalized, that the properties of a copolymer are approximately the additive properties of the homopolymers. This should not be interpreted, however, as meaning that blends of the homopolymers will yield comparable results. Such a result, as a matter of experience, would be the exception rather than the rule since, in many cases, blends of the homopolymers are not even compatible.

D. Compounding vs. Polymerization

The requirements of leather finishing are manifold and many minor modifications in gloss, plating, softness, etc., may be achieved most readily by suitable compounding methods. Improved plating, for example, can be obtained by the use of small amounts of waxes, shellacs, caseins, etc., without affecting other requirements adversely. However, it should be emphasized that this approach may result in significant variations in other important properties if compounding is carried out to an extreme such as when an effort is made to use a single or even several resin emulsions as the basis for many diverse applications.

Over many years, it has been the experience of our group that the same generic problems arise in the field. It has been our approach to attack this type of problem on a fundamental basis, since the facts gleaned from a research program of this type always expedite the solution of field problems as they arise.

The remainder of this paper is devoted to the highlights of several of these investigations with particular reference to the relative merits of compounding and choice of resin emulsion.

1 Plating

This problem was chosen for investigation not only because it is a universal finishing technique but because the problem of "sticking" at high temperatures and pressures is prevalent in most tanneries.

It is our intent to develop a complete understanding of the compounding technique as well as the study of new copolymers to solve this problem.

One series of experiments was carried out to determine the interaction of the following variables in base coat formulations: maximum plating temperatures, compounding ingredients and resin emulsion type.

One type of snuffed leather was taken for all experiments. Two base coats were applied using this standard formulation:

1 part Pigment Dispersion (Standard Pigment Finish)
1 part Resin Emulsion at 25 per cent Solids
1 Part Water

Two coats were applied by hand swab, dried between coats, then plated. This same technique was used on all tests.

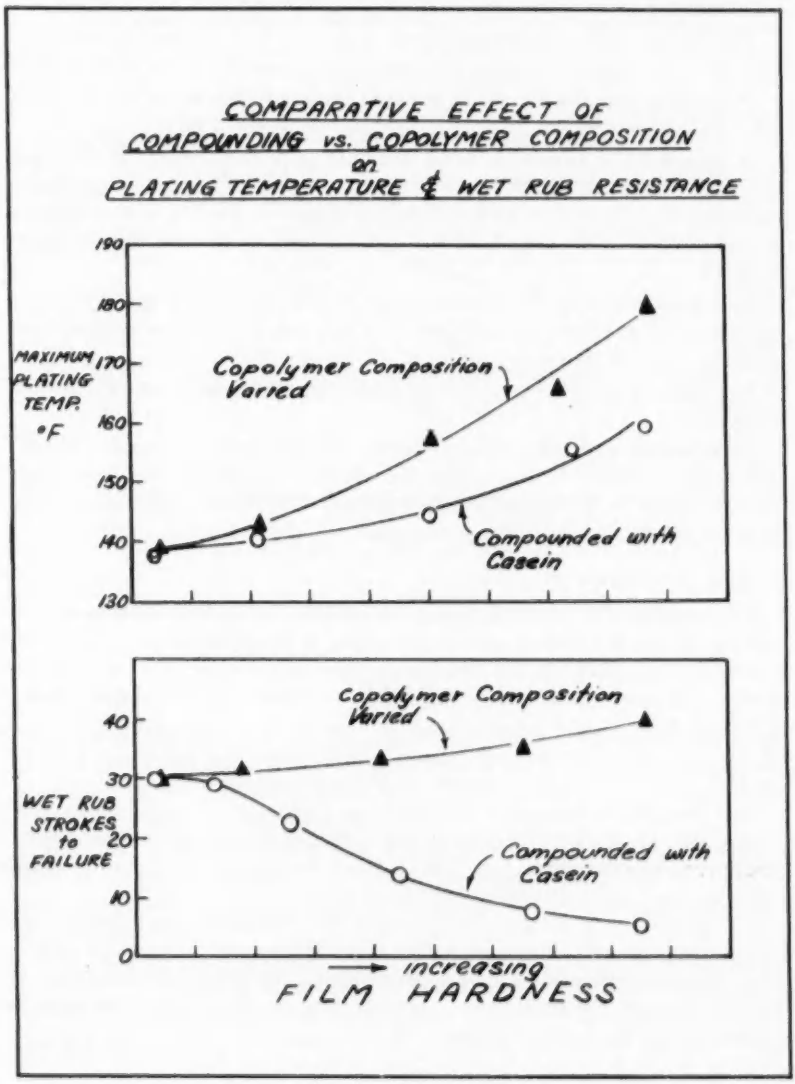

FIGURE 1

In Fig. I "Maximum Plating Temperature" is defined as that temperature at which sticking to the plate occurred at 8000 psi. on a laboratory model Carver press.

"Wet Rub Strokes to Failure" was measured by a cloth covered mechanical device kept wet throughout the measurement. Break through of the finish was observed when the leather itself was first noticed.

The compounding ingredients were identical but continually increased and the resin emulsion system was maintained except for the monomer ratio.

Fig. 1 illustrates the use of a 10 per cent casein solution as the compounding ingredient.

It should be particularly noted that the wet rub resistance decreased drastically with increased casein content, whereas a change in copolymer increased the wet rub resistance slightly. Moreover, the "Maximum Plating Temperatures" at the same hardness were uniformly higher for the copolymer systems.

This same series of experiments were tried using other compounding ingredients, for example; different types of wax emulsions, soap solutions and different types of gums, etc.

Although the graphs were different in all cases, the same overall generalizations held.

Experiments were also carried out to determine differences in "break" under the varying conditions outlined above. It was our conclusion that "break" could be better controlled by proper selection of copolymer system than by simple compounding techniques.

II Low Temperature Flexibility

This problem was initiated during World War II when the development of finishes for leather jackets and shoes for use in extremely cold climates was extremely important. It was also felt that the information afforded from this work would prove useful in solving similar problems for civilian applications.

One of the obvious methods for improving the low temperature flexibility of any synthetic resin is to incorporate plasticizers of various types to soften the film. This constituted a portion of the early work on this project.

The cracking temperature mentioned in Figure II was obtained by subjecting individual pieces of finished and conditioned garment leather to propressively lower temperatures. The recorded temperature was that at which the finish just began to crack under rapid flexing.

In Figure II, the cracking temperature was materially improved by the increase in plasticizer content as well as by modifications in the acrylic copolymer. However, on aging at room temperature, the plasticizer lost much of its effectiveness presumably by migration into the leather or slow volatilization whereas the copolymer was unaffected.

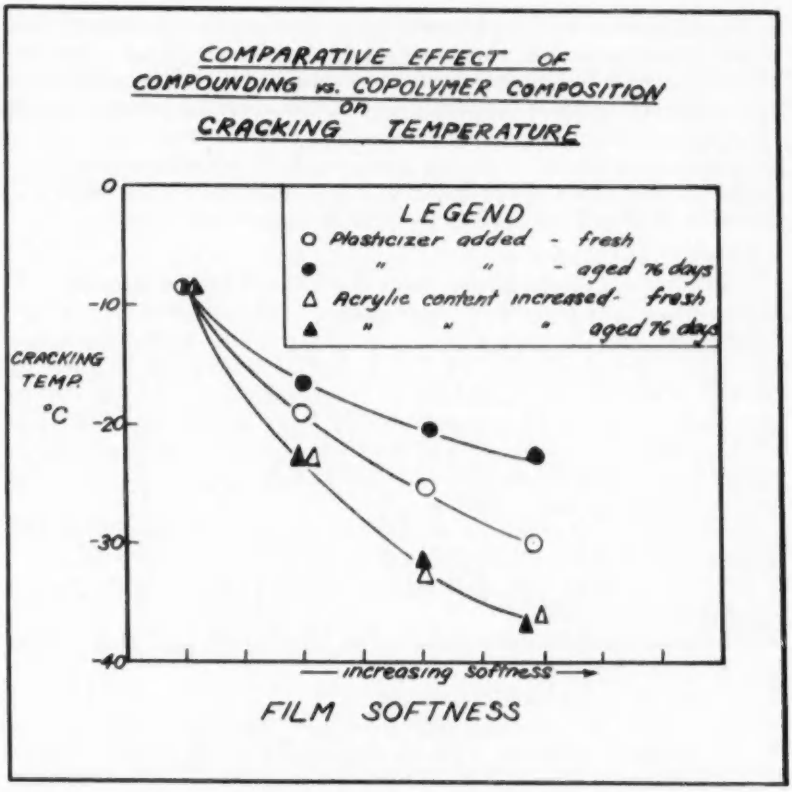

FIGURE 2

III Penetration and Leveling

The proper application characteristics of a leather finish are as important to the ultimate appearance as are the quality of the leather and the skill and experience of the finisher. Streaks, variations in gloss and levelness are all symptoms of poor application qualities.

Although the problems relating to the penetration and leveling of a leather finish are usually controlled by acceptable compounding techniques, it is often possible to minimize compounding by suitably adjusting the polymerization recipe.

Since wetting agents and colloids are the conventional addends for improved application qualities, it would appear simple to increase the wetting agent content in a polymerization system and thus obtain improved leveling characteristics. Unfortunately, this apparent simplicity is misleading.

In the course of an emulsion polymerization, the emulsifiers become absorbed in the polymer particles. Increasing the amount of wetting agent increases the total particle surface area by forming many more smaller particles and the added wetting agent becomes absorbed. However, by suitably varying the polymerization technique such that the particle size does not decrease or by utilizing emulsifying or wetting agents which are not efficiently absorbed on the polymer particle (the non-ionics) it is possible to prepare a resin emulsion with improved leveling and penetrating characteristics.

IV Gloss

In general, it is most desirable that a leather finish be formulated to yield a gloss which does not change upon plating. The realization of this ideal finish would minimize uneven gloss, give a more natural leather appearance and permit plating to be used for its true purpose of smoothing and leveling the leather surface. The main difficulty in achieving this goal lies in the fact that gloss is primarily a function of film continuity and the compatibility of the components. In common with most thermoplastics, the resins used in leather finishes form a more continuous film at high temperatures and, therefore, the gloss increases on plating.

As a practical goal, it is more realistic to attempt to minimize the increase in gloss upon plating realizing that some increase will inevitably occur.

Thus, the following techniques may be employed to improve the gloss of the base resin emulsion.

1. Improve continuous film formation by lowering the particle size. This may be accomplished by
   a. Increasing the emulsifier content
   b. Utilizing a polymerization technique (monomer addition)[4] in which the monomer is always polymerizing in a large excess of emulsifier
   c. Use a polymerization recipe balanced with regard to salts, colloids, etc., which leads to minimum particle size.
2. Improve compatibility of the system by screening all the emulsion ingredients for mutual compatibility. No fundamental rules can serve as guides in this case; experience is the only answer

The final compounding of the leather finish, of course, must not cause particle agglomeration nor should the ingredients be incompatible.

Conclusion

A knowledge of the fundamentals of emulsion polymerization has been shown to be of general value in the formulation of leather finishes to obtain particular characteristics. It has also been noted that exceptional versatility is available to the leather finish industry in the variations of properties which can be obtained by the myriad resin emulsions which are, or can be, manufactured.

It is hoped that this paper has contributed in some small way to a better understanding of the mutual problems of the emulsion manufacturer, the finish manufacturer and the finisher in the tannery.

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DISCUSSION

Dr. Robert Shaw (Rohm & Haas): I would like to congratulate Dr. Naidus on a very fine paper and on a subject which I do not believe has been discussed at these meetings before.

I think you will realize from the charts which he has shown, particularly the charts with the different monomers, that you can make a tremendous variety of polymers; that actually there is no limit to the number of resinous materials which can be made and which might be useful in leather finishing.

In fact, the trouble with all of these new polymers is that the high polymer chemist can make these a lot faster than one can evaluate them. It is a question of trying to select, and I think Dr. Naidus has shown how we have good reason to select certain polymers as the best ones and try to improve these as best we can.

One point I would like to make in connection with this is that while we can change the physical properties of a resin by the methods which Dr. Naidus has mentioned, the hardest thing in the world I think is to change just one property. Because when you change one property you get a corresponding change in another property. And it is a question of juggling all of these things to come out with the advantage in the property you are looking for, and not too much disadvantage in other properties.

I have one question I would like to ask Dr. Naidus in connection with the graphs he showed relating hardness to plating temperature and wet rub resistance.

The question is: Was the hardness measured by any means, or was this deduced from a knowledge of the composition which you had?

Dr. Naidus: Within the co-polymer system, itself of course, we know we were getting harder and harder. We know the direction in which we were going. But we did measure, with a modified Shore hardness tester, the hardness of the co-polymer system and the compound system.

Shaw: I noticed the points for casein additions and the different co-polymers were one above the other.

Naidus: That has no significance, really. We simply chose an area in which we had approximately the same properties, because we were trying to get

generalizations. This has not been pinpointed in a detailed sense at all.

SHAW: Thank you. I would like Mr. Stahl to continue this discussion now.

MR. LOUIS E. STAHL: (Stahl Finish Company): In deference to the time I will forego any discussion and plunge right into the question period. Are there any questions?

DR. HOLLOWAY: (R and M Industrial Laboratories) I wonder if Dr. Naidus will discuss the effect of particle size on the emulsion—as to gloss and plating temperature.

NAIDUS: Particle size is one of the most significant properties in an emulsion polymer. To discuss it in general is a difficult thing, but I would say this: continuity of film is an important aspect for achieving optimum gloss. The finer the particle size, the more contacts the particles have in the emulsion, the less open spaces there are and the better continuity you get. Thus, one would want the finest possible particle size.

On the other hand, if you consider filling and penetration, if you have too fine a particle size, the resin emulsion might penetrate into the leather too deeply; although you would want a certain amount of penetration for good adhesion.

If your particle size was too great, you would have poorer film continuity and resultant pigment binding problems.

So there is an optimum particle size when you are considering properties such as filling or coverage with a resin.

HOLLOWAY: Relative to adhesion, where you determine adhesion as in butadiene-styrene to nitrocellulose, what is the determining factor in the adhesion properties—is it the base polymers themselves or some of the additives and emulsifying materials you use in the systems?

NAIDUS: I think with respect to adhesion, that within the limits of emulsifier quantities that are normally used in emulsion polymerization, they would have little effect. Adhesion is a function of the polymer itself and it simply happens that styrene-butadiene does not have good compatibility with nitrocellulose and therefore does not have good adhesion.

You could improve it by putting in a plasticizer. But it is the base polymer which is the primary material with respect to adhesion.

MR. ARTHUR GOETZ (Good Leather): Dr. Naidus, will you spend a few moments on the influence of the type of fatliquor on these finishes—particularly adhesion and cold temperature?

NAIDUS: We anticipated such a question but the type of fundamental work which I mentioned we had started and are continuing to do, has not yet allowed us to branch too far in terms of the type of leather we are using, or the type of tannage. We do know, of course, there is a significant difference, and I think perhaps Mr. Stahl might have a few remarks to make on that.

STAHL: Well, we have done a great deal of work and have considerable

data on the effects of certain type resins on vegetable tanning and on chrome re-tan tanning, and also the effect of these resin emulsion finishes on the new type of resin tannage.

I do not think I could discuss this thing in one or two minutes, but at some later time I think we shall present a paper on the effects of certain types of resins to definite tannages and definite fatliquors, and definite leathers. I hope that satisfies you, right now.

MR. JAMES M. CASSEL (National Bureau of Standards): I would like to ask regarding the freeze-thaw stability of resins. Do all resins act the same way or are some resins more stable to coming back?

NAIDUS: Unquestionably certain resins are more freeze-thaw stable and others are completely non-freeze thaw stable. In general, the interest in this is with consumer goods—the new latex paints, for example. It has not arisen particularly in the leather finish industry. However, there are some generalizations that can be made with respect to freeze-thaw stability. It appears as if the more stable the emulsion system with respect to mechanical stability, with respect to heavy metal ions, to salt, to pH, etc. the more likely you are to have a material which is freeze-thaw stable. The usual additives, such as casein, shellac, and so on, will generally contribute. They make take a material which is not in itself freeze-thaw stable and shove it over the border and make it freeze-thaw stable.

MR. CLINTON E. RETZSCH (Nopco Chemical Company): I would like to ask this regarding your testing of a finish that would stand up under low cold test; what relation have you found in obtaining satisfactory results with the use of a low cold test oil as a fatliquor prior to the finishing?

NAIDUS: Again it is pretty much the same answer as we made to the other gentleman. We have not as yet been able to spend as much time as, of course, we would like to spend, with respect to the problems of the changes in treatment of the leather prior to finishing. At the present time we have restricted ourselves, certainly for presentation, to a particular type of leather. We have done a good deal of work on the others but we are not ready to present any data. We do not feel that we have anything that we would even like to generalize on.

STAHL: I would like to add to that. We found that in the cold temperature flexibility of leather, that the leather, itself, plays a very important part. We have found that certain resins that do not exhibit good cold temperature flexibility and go down to the range of -30°F if you put them on certain types of garment leather, the leather and the finish itself will withstand -60°F.

It is our conclusion that the leather does help a great deal perhaps because of the low temperature oil that you have in there.

If there are no further questions, I would like to thank Dr. Naidus for his talk, and also you gentlemen for receiving it so well.

A Comparison of Gas Chamber Tests of Bookbinding Leather With a Long Time Atmospheric Exposure

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Abstract

Twenty-four samples of bookbinding leathers, tanned in various ways, have been exposed as bookbindings to atmospheric pollution for periods of 12 to 19 years. Physical and chemical tests made after exposure correlate reasonably well with gas chamber tests made on the leather before exposure.

Introduction

The deterioration of bookbinding, upholstering and similar leathers has been the subject ot many investigations. A bibliography of some of this work is given at the end of the paper.

Veitch, Frey and Leinbach [44] in 1926, and Innes [22] in 1930 published data indicating that the pick-up of sulfuric acid from polluted atmospheres was an important cause of the decay of leather bindings. This was confirmed in 1931 by Frey and Clarke [16], who showed that leathers absorbed from the air the equivalent of 2 to 8 per cent sulfuric acid in about 8 years.

In previous work on the deterioration of bookbinding leathers we have used a gas chamber as a means of increasing the concentration of SO_2 gas in the atmosphere. Gas chambers had previously been used by Woodward [46], and Lamb [36].

In our original gas chamber [17] pollution of the atmosphere was caused by a lighted gas jet burning continuously at the rate of 2.17 cubic feet per hour. The sulfur content of the gas was such that the gaseous sulfur products of combustion ranged from 0.00088 to 0.00101 grams per 100 liters of air, calculated as H_2SO_4. Under these conditions the deterioration or "red-rotting" of vegetable-tanned leathers in 12 to 18 weeks was strikingly similar to that obtained under natural conditions over several years. Results obtained by physical and chemical tests were also similar to those obtained with naturally deteriorated leather.

The pollution of the atmosphere in this type of chamber depends upon the sulfur content of the illuminating gas which varies widely from place to place. Therefore, a new type of gas chamber [19] was devised in which the amount of pollution could be rigidly controlled. The pollution depended upon the

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burning of methanol containing dissolved amyl sulfite. A lamp was developed which gives a uniform sized flame at all times and which requires filling only once a week. For our work the lamp was adjusted to burn 95 grams of fuel in 24 hours, giving 1.78 grams SO_3, and a concentration of SO_2 in the chamber approximately the same as in the illuminating gas chamber.

Innes, Mayer and Mitton have recently devised a gas chamber[26]. This contains several modifications but the fundamental feature is the same as in our gas chamber, that is, the production of an SO_2 polluted atmosphere by the burning of a fuel containing sulfur in some form.

With our gas chamber we have determined the resistance to acid deterioration of leathers tanned by different tanning materials[18], by straight chrome tannage[17], and by combination tannages such as chrome and vegetable[15] and vegetable and alum[6, 19]. We have also determined the effect of adding materials to the leather such as sodium chloride, natural non-tannins and buffering salts[18]. We found that chrome-tanned leather was more resistant than vegetable-tanned. However, chrome-tanned leather is more empty, stretchy and resilient than vegetable-tanned; it resists wetting back uniformly with water and is difficult to dye and finish as compared with vegetable-tanned leather. These properties make it somewhat unsuitable for bindings. A combination chrome and vegetable tanned leather retains many of the desirable properties of vegetable-tanned leather and also has some of the acid-resistant properties of the chrome-tanned leather. Later it was found that vegetable leathers retanned with alum[6, 19] were equally satisfactory.

For an evaluation of the value of the gas chamber tests, it was desirable to obtain a comparison of the results obtained by it, and those obtained by actual exposure. The results of such a test, requiring several years, are described in this paper.

Experimental

The experimental work was carried out in collaboration with the Government Printing Office. During the period from 1935 to 1941 twenty-four skins were obtained, tanned in various manners. Enough of each of these skins was cut out for exposure in the gas chamber, followed by physical and chemical tests. The remainder of each skin was then sent to the Government Printing Office where 3 volumes were bound with it. One set of these volumes was placed in a bookcase at the Government Printing Office and subjected to the natural pollution of the Washington atmosphere. The other books were returned to the laboratory, where each was carefully wrapped in waxed paper to prevent access of air, and kept in this condition until tested.

The leathers used were 21 chrome-vegetable-tanned, 2 alum-vegetable-tanned and one vegetable-tanned as follows:

Volume No.	Type	When exposed
1	Combination vegetable-chrome sheepskin	Dec. 20, 1934
2	Combination vegetable-chrome sheepskin	Jan. 11, 1935
3	Combination vegetable-chrome sheepskin	Feb. 26, 1935
4	Full chrome sheepskin	Apr. 12, 1935
5	Full chrome sheepskin	May, 1935
6	Full chrome sheepskin	Feb., 1936
7	Combination vegetable-chrome goatskin	May, 1936
8	Combination vegetable-chrome goatskin	Aug., 1936
9	Full chrome goatskin	Aug., 1936
10	Combination vegetable-chrome goatskin	Sept., 1936
11	Full chrome cowhide	March, 1937
12	Combination vegetable-chrome cowhide	Nov., 1937
13	Combination vegetable-chrome goatskin	Nov., 1937
14	Combination vegetable-chrome goatskin	Nov., 1937
15	Combination vegetable-chrome sheepskin	Dec., 1937
16	Combination vegetable-chrome cowhide	Jan., 1938
17	Combination vegetable-chrome goatskin	May, 1938
18	Full chrome goatskin	May, 1938
19	Full chrome goatskin	Aug., 1938
20	Combination vegetable-chrome cowhide	Oct., 1938
21	Vegetable-tanned eastern sharkskin	March, 1939
22	Combination vegetable-chrome sheepskin	July, 1939
23	Combination vegetable-alum sheepskin	Sept., 1941
24	Combination vegetable-alum sheepskin	Sept., 1941

The volumes exposed to atmospheric pollution were returned to the laboratory in 1953. The bindings were removed and examined. The visible effects of deterioration are reported in table I, as compared with protected bindings.

Tensile strength determinations were made of the leather from the backs of the bindings which had been exposed. The results were compared with the tensile strength of the original leathers. This introduces large sources of error. The strips of leather available allowed only 3 or 4 test samples to be taken. This small number of samples cannot be taken as representative. Another error is caused by the effects of the finish on the leather, which might give a considerable protection to the naturally exposed leather, and only slight protection to the gas chamber pieces which were exposed on all sides. A further source of error is the variation in strength between different portions of the same skin. It is improbable that the portion of the skin used for binding would be adjacent to the strip used for the original tensile strength determinations, therefore, the basis for the comparison would be faulty. In a few cases, we were able to obtain a more accurate comparison because

TABLE I

Comparison of Exposed and Protected Leathers

	Color		Crackiness	
	Protected Leather	Exposed Leather	Protected Leather	Exposed Leather
1	Light tan	Dirty yellow	Slight	Slight
2	Light tan	Dirty brown	Not cracky	Not cracky
3	Cream	Brownish white	Not cracky	Not cracky
4	Light tan-pinkish	Dirty white	Not cracky	Slight
5	Light tan-pinkish	Dirty brown	Not cracky	Not cracky
6	Tan-pinkish	Dirty white	Not cracky	Not cracky
7	Bluish black	Brown	Not cracky	Not cracky
8	Red	Dull reddish brown	Not cracky	Not cracky
9	Red	Somewhat faded	Not cracky	Not cracky
10	Red	Somewhat faded	Slightly cracked	Slightly cracky
11	Red	Red with white undertone	Not cracky	Not cracky
12	Red	Red-unaffected	Not cracky	Not cracky
13	Red	Red-dull	Not cracky	Not cracky
14	Blue-black	Brown-black	Not cracky	Not cracky
15	Tan	Little changed-dull	Not cracky	Not cracky
16	Green	Little changed-dull	Not cracky	Not cracky
17	Brown	Brown-no change	Not cracky	Grain slightly cracky
18	Black	Black-no change	Not cracky	Not cracky
19	Black	Dull black	Not cracky	Not cracky
20	Black	Dull black	Not cracky	Slightly cracky
21	Black	Reddish black (red rot)	Not cracky	Very cracky
22	Tan	Dull tan	Not cracky	Not cracky
23	Red	Red (little change)	Not cracky	Not cracky
24	Blue	Blue (little change)	Not cracky	Not cracky

pieces of the original skin adjacent to the part used for the binding had been preserved, and in other cases, protected pieces from the sides of the bindings were used for control. On the whole, however, no close correlation should be expected between the comparison of tensile strengths before and after exposure.

Chemical tests consisted in the determination of pH, soluble nitrogen and total sulfur. The pH was determined by the official methods of the American Leather Chemists' Association [1]. For determination of soluble nitrogen, one gram of leather was leached with 100 ml. of water at 50°C., then with N/10 Na_2CO_3 at room temperature. Soluble nitrogen is the sum of the nitrogen in the solutions expressed as a percentage of the original leather. Total sulfur was determined by the bomb method [8] and reported as per cent of H_2SO_4 on the original leather.

TABLE II

Data for Deteriorated Leather

Binding No.	Cr_2O_3(1) or Al_2O_3	Initial Strength Lbs./sq. in.	Deterioration Gas Chamber(2) %	Deterioration Natural Exposure %	Time of Natural Exposure Years	pH Initial	pH Gas(2) Chamber	pH Natural Exposure	Sulfur Pickup as H_2SO_4(3) Gas Chamber %	Sulfur Pickup as H_2SO_4(3) Natural Exposure %	Soluble Gas(2) Chamber %	Nitrogen(3) Natural Expsoure %
1	3.0	1770	56.5	43.5	19	3.18	2.19	2.70	2.7	2.1	1.9	0.6
2	4.5	3420	46.3	41.2	18	4.57	2.40	2.62	3.0	1.7	0.6	0.4
3	4.6	4730	24.6	25.5	18	5.69	3.34	3.59	1.5	1.7	0.3	0.7
4	4.9	1850	27.7	31.7	18	4.34	2.75	3.34	1.7	1.1	0.2	0.7
5	3.4	4130	40.7	58.3	18	4.33	3.13	3.28	2.6	2.2	0.1	0.6
6	4.6	3450	10.6	19.0	17	4.95	2.93	3.50	1.0	1.5	0.3	0.6
7	2.0	5350	51.4	70.3	17	3.48	2.27	2.42	4.2	1.2	1.4	1.1
8	2.2	4950	50.2	62.4	17	4.45	2.23	2.75	4.6	1.5	0.6	0.7
9	4.3	6300	32.5	21.8	17	4.04	2.75	3.02	2.4	1.5	0.1	0.4
10	2.5	2530	39.5	56.9	17	4.33	2.53	2.55	2.1	2.3	0.8	1.7
11	3.0	2690	18.9	20.8	16	4.34	3.30	3.45	1.6	0.9	0.3	0.8
12	2.2	1370	28.7	6.1	16	3.79	2.27	3.20	3.6	2.4	0.5	0.4
13	2.5	6180	55.8	65.5	16	3.32	2.14	2.60	3.9	1.9	0.7	0.4
14	2.3	5740	51.7	61.3	16	3.39	2.25	2.58	3.7	2.0	0.9	0.3
15	1.1	2170	45.5	45.0	16	3.51	2.13	2.90	3.6	2.0	1.1	0.5
16	1.9	2630	52.9	31.5	15	4.07	2.26	3.10	2.9	1.9	1.7	0.5
17	1.0	5620	78.5	35.5	15	6.08	2.17	2.95	4.9	1.7	1.8	0.6
18	4.7	4600	25.1	53.9	15	4.17	2.73	2.92	3.9	2.8	0.5	0.5
19	2.7	7020	38.3	40.3	15	5.14	2.40	2.97	3.5	1.2	0.4	0.4
20	0.9	2010	46.4	36.8	15	3.28	2.16	2.93	3.7	2.5	0.7	0.4
21	None	1050	71.4	61.9	15	3.18	2.16	2.21	4.0	3.1	4.9	3.3
22	2.1	2670	46.5	65.9	14	3.12	2.14	2.65	3.2	2.1	0.8	0.5
23	2.3	1770	10.3	22.6	12	4.11	3.56	3.90	1.9	0.7	0.3	0.4
24	2.3	2680	7.1	7.9	12	4.16	3.60	3.92	1.0	1.5	0.2	0.3

(1) Leather 21 was vegetable tanned; 23 and 24 vegetable leathers retanned with alum; the rest of the leathers are chrome or combination chrome vegetable leathers.
(2) Gas chamber data are for 12 weeks exposure.
(3) Calculated as per cent of original leather.

Table II gives the results of the physical and chemical tests as compared with similar results obtained on the leather exposed in the gas chamber for 12 weeks.

Discussion

The exposure period of the bindings ranged from 12 to 19 years. Therefore, a ranking of the volumes for durability is not absolutely accurate, but the results should be fairly conclusive. In the following table the volumes are ranked in the order of decreasing resistance as shown by the gas chamber and by atmospheric exposure.

Ranking of Leather in Order of Decreasing Resistance as Measured by Tensile Strength

Volume No.	Ranking Gas Chamber	Bindings	Volume No.	Ranking Gas Chamber	Bindings	Volume No.	Ranking Gas Chamber	Bindings
1	22	14	9	9	5	17	24	10
2	14	13	10	11	18	18	6	16
3	5	7	11	4	4	19	10	11
4	7	9	12	8	1	20	15	12
5	12	17	13	21	22	21	23	20
6	3	3	14	19	19	22	16	23
7	18	24	15	13	15	23	2	6
8	17	21	16	20	8	24	1	2

TABLE III

Evaluation of Ranking Data

To evaluate the data we used a nonparametric test proposed by Kendall and Smith[33], as modified by the Frankford Arsenal[14].

The relative rankings and their sums were taken as follows:

Gas Chamber				22	14	5	7	12	3	18	17	9	11
Natural Exposure				14	13	7	9	17	3	24	21	5	18
Sum				36	27	12	16	29	6	42	38	14	29
4	8	21	19	13	20	24	6	10	15	23	16	2	1
4	1	22	19	15	8	10	16	11	12	20	23	6	2
8	9	43	38	28	28	34	22	21	27	43	39	8	3

The mean is $\frac{m(n+1)}{2} = \frac{2(25)}{2} = 25$

where m = number of methods of test = 2 (gas chamber and natural exposure).

n = number of samples = 24

S — sum of the squares of the differences between the mean and the separate sums = $11^2 + 2^2 + 13^2$ — etc. = 3806

$$w = \frac{12s}{m^2(n^3-n)} = 0.827$$

The Snedecor F value was calculated as proposed by the Frankford Arsenal Manual.

$F = \frac{A}{B}$ Where A = (n-1)w and B = 1-w.

$$\frac{A}{B} = 109.9$$

The degrees of freedom for $A = (n\text{-}1) - \frac{2}{m} = 22$

The degrees of freedom for $B = (m\text{-}1)\ (n\text{-}1) - \frac{2}{m} = 22.$

From the table the F values for the 5% and 1% level are: $F_{.05} = 2.05$ $F_{.01} = 2.79$
A comparison of these values with the F value as determined indicates that there is good agreement between the two methods of test.

A non-parametric analysis of these results (table III) shows a Snedecor F value of 109.9 as compared with 2.05 at the 5 per cent level and 2.79 at the 1 per cent level. This shows good agreement between the two test methods. Table II shows that sulfur pick-ups are close to what would be predicted.

Corroborating results of previous tests, it is seen that the amount of soluble nitrogen for semi-chrome or alum leathers is not a satisfactory criterion of deterioration. All pH figures for the exposed bindings are higher than anticipated. We can give no satisfactory explanation for this.

The results of the two alum-retanned leathers are of particular interest. Although the exposure period is not as long as for some of the other leathers, it is still long enough to give a fair indication of the value of the tannage. The deterioration is small, as predicted by gas chamber tests. As measured by the peroxide test or the bomb test, the resistance of this type of leather is low.

In considering the mechanism of the deterioration of leather exposed to atmospheric pollution, it has been established that the leather absorbs sulfur dioxide from the air, which is oxidized in the leather to sulfuric acid. This oxidation may be accelerated by the presence of iron or other metals. The sulfuric acid degrades the protein by hydrolysis which is accompanied by oxidation. It has been assumed that oxidation as well as hydrolysis is necessary to produce the deterioration. This assumption is supported by the fact that oxidation as well as hydrolysis is required to give to deteriorated vegetable leathers the typical appearance of "red rot". Further, the amount of ammonia produced is too large to be accounted for by simple hydrolysis without oxidation. However, these facts can be as satisfactorily explained by assuming that oxidation is a secondary phenomenon acting only on proteins partly degraded by hydrolysis. In support of this assumption, it is found that mineral tanned leather or combination mineral-vegetable tanned leather may undergo as much as 40 per cent deterioration with the formation of only negligible amounts of ammonia. In this case, only small amounts of soluble nitrogen are formed. This is explained by Kuntzel[35] as follows: "It is probable that this decomposing action is not limited only to the splitting

of soluble protein fragments from the insoluble protein system but that also the insoluble remainder of the fibre system undergoes decomposition, leading to a diminution of tensile strength. On this view, in the course of the acid action the collagen undergoes a mild hydrolytic fission of such a nature that the whole system of molecules, bound by main and auxiliary valences, does not as such fall to pieces."

The results of the gas chamber test do not depend upon any assumption regarding the mechanism of the reaction involved. The only assumption made is that in accentuating the normal conditions of atmospheric pollution, the reactions involved will proceed in the same course at an accelerated rate. The gas chamber gives very valuable results in evaluating the results of leather treatments where the treatment is the only variable involved. The results are not as satisfactory in comparisons of different leathers, where other factors, such as thickness or different types of protective coatings, are involved.

Two methods have been devised for evaluating the resistance of leather to acid deterioration based on the assumption that oxidation is the principal factor in the action. In the method of Innes[24] sulfuric acid is added to leather in a sufficient quantity to give 5 per cent on the weight of the dry leather. After drying, hydrogen peroxide is added, in 6 additions, with intermediate drying in the proportion of 0.6 ml of 10 volume hydrogen peroxide per gram of leather. Deterioration is judged by cracking, blackening, gelatinization or the production of holes in the leather.

In the method devised by Kanagy[27], of the U. S. Bureau of Standards, leather is heated to 100°C. in an oxygen bomb, without any addition of acid.

A comparison of the peroxide, gas chamber, and oxygen bomb methods was published in 1944[13]. This was the result of collaborative work between the British Leather Manufacturers Association, represented by R. F. Innes; the Bureau of Chemistry and Soils of the U. S. Department of Agriculture, represented by R. W. Frey, C. W. Beebe, and J. S. Rogers; and the Bureau of Standards of the U. S. Department of Commerce, represented by R. C. Bowker and J. R. Kanagy. The conclusions derived from this comparison were:

1. "Acid deterioration is the main cause for the failure of leathers normally expected to give many years of service. If the leather is made with a sufficiently high pH and no further acid has been deliberately added, then the acid causing deterioration evidently has been absorbed from polluted atmospheres.

2. "The rate of deterioration of leathers resulting from the absorption of acids from the atmosphere is dependent upon three main factors: (a) rate of absorption of acid from air, which may be greatly influenced by methods

of finishing, (b) effect of absorbed acid in reducing the pH of the leather, in which action differences in buffering capacity play an important part, and (c) the rate of action of the acid on leather at a definite pH. Each of these factors varies with different leathers.

3. "The gas chamber test is the most satisfactory method for measuring resistance to acid deterioration, but cannot be used to evaluate deterioration caused by other factors. Theoretically, the criterion of percentage soluble nitrogen should be the basis of assessment since it indicates break down of the tanned collagen, but loss in tensile strength is found practically to be superior if enough of the sample is properly selected and used. It is a more sensitive criterion since a measurable loss in tensile strength may be observed before the sample has deteriorated sufficiently to give a measurable change in the amount of nitrogenous material extractable. It has also been shown that combination leathers give abnormally low values in soluble nitrogenous materials, and, in the case of leathers tanned partly or wholly with chromium, alum or other mineral agents, it is thought that the loss in tensile strength indicates most nearly the correct degree of deterioration.

4. "There is a marked parallelism in the durability of the leathers as judged by the gas chamber and peroxide tests. Both show that sodium lactate, formate and chloride have a marked protective action but the peroxide test has its limitation, particularly in that it causes an unequal distribution of acid in the leather. It is also of no use for combination chrome-vegetable leathers which are growing in importance on account of their durability. The peroxide test gave much deterioration because it introduced more mineral acid than that which was absorbed by this particular leather in the gas chamber test.

5. "Oxidation tests determine reactivity of leather to oxygen under standard conditions and the rate of oxidation apparently varies under different conditions. The reactivity to acid is not necessarily the same as the reactivity to oxygen. No account is taken of the presence of buffering materials which actually neutralize acid as it is absorbed and no account is taken of the rate of absorption of acid. Thus, the oxygen bomb test is not satisfactory as a forecast of durability in acid atmospheres because the leathers do not become acid and it gives quite different results from the other two tests. The native tanned Nigerian goatskin shows less deterioration after removing the water solubles. The quebracho-tanned leather shows as good durability as the sumac-tanned leather. These findings are at variance with practical experience and published research in this connection.

6. "Buffering capacity is no criterion of durability. The following table (*for table see original text*) [18] shows that resistance to the gas chamber and

peroxide tests does not run parallel with buffering capacity. This might be expected because durability is also determined by the rate of absorption of acid from the air and the rate of action of the acid on leather at a definite pH. Buffering capacity also does not take in account protection provided by such materials as sodium chloride which do not affect pH, reactivity or rate of absorption."

The explanation of the fifth conclusion is that this test was devised for a normal atmosphere and not for one containing acid fumes. Kanagy [13] states "We recognize the damaging effects of sulfur dioxide fumes but we believe that by using leather having a satisfactory initial pH and with the aid of modern methods of air conditioning this factor can be practically eliminated." Burton took issue with this statement as far as England is concerned with the opinion that sulfur dioxide pollution was still a major problem. It is our opinion that in this country also atmospheric pollution is a major problem of increasing importance and many bookbindings are not protected by air-conditioning. If results from these tests are extended to upholstery leather, the protection given by air-conditioning is of a still smaller extent.

Innes, Mayer and Mitton have tested 8 leathers in their gas chamber [26]. In the comparison of the leathers after exposure, alum-treated leather ranked first by gas chamber tests, but only sixth by the peroxide or bomb test. As the rating given by their gas chamber confirms the results of our gas chamber, and further, as these results are corroborated by the actual exposure tests reported in this paper, it would appear that the ratings given by the peroxide or bomb tests are erroneous. Apparently, the peroxide test is unsatisfactory for vegetable-alum leathers as well as for chrome-vegetable leathers.

Conclusions

Results of actual exposure of leather for 11 to 19 years confirm reasonably closely the predictions made by gas chamber tests of the original leather.

The soluble nitrogen content of deteriorated combination vegetable and mineral leather is not a satisfactory criterion of the amount of deterioration.

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ABSTRACTS

Corrosion In the Tannery. By F. E. Humphreys. *Corrosion Technology*, **2,** No. 6, (1955). The atmosphere of a tannery is one of the most highly corrosive of industrial atmospheres. Humidity is high, often containing corrosive vapors from the various liquors used in tanning processes, and the tanner has to choose his metal materials carefully. An additional hazard is the danger of harmful corrosion products dropping on to the skins and hides. This article describes metals which can be used for different tanning processes and also methods of protecting structural steelwork of the tannery. Staybrite steel (a steel containing 18/8% Cr/Ni and Mo.) is recommended for practically all the various tanning processes including soak liquors, lime liquors, deliming and bating liquors, pickle liquors, vegetable tannin liquors, chrome tannin liquors and for those metal portions of wooden drums. Also staybrite steel rollers are said to impart a higher polish to leather than bronze, which develops slight pitting in use. In the use of coatings for the protection of structural steelwork, chlorinated rubber systems, in general, gave poorer results than linseed oil paints. Of the paint systems tried, none gave longer life than a linseed oil based system with a red lead undercoat and an excluding top coat, a result with which other investigators agree. The composition of the primer coat is highly important. Metallic

lead and calcium plumbate seemed comparable to red lead. Metallic zinc and zinc chromate were inferior to red lead, although in less corrosive atmospheres good results were obtained. The failure of zinc rich primers in this very corrosive atmosphere may have been due to the impossibility of obtaining a substantial area of metallic iron/zinc contact. The failure of Chlorinated rubber and synthetic systems was probably due to failure of the primer. R.B.K.

Measurements of the Heats of Wetting of Leather. By R. G. Mitton and R. J. Mawhinney. *J. Soc. Leather Trades' Chemists*, **39**, 206 (1955). The integral and differential heats of wetting of a chrome- and a vegetable-tanned leather were measured calorimetrically. The heat of wetting was determined by comparing the rise in temperature caused by the wetting of a specimen with that caused by a known input of electrical energy. Dry specimens were obtained by drying for at least 10 weeks over sulfuric acid in a vacuum desiccator. Samples with varying amounts of moisture were obtained by equilibrating over sulfuric acid or saturated salt solutions giving relative humidities between 2 per cent and 92 per cent. At zero moisture content, the integral heat of wetting of chrome-tanned leather (40.6 cal./g.) was greatly in excess of that of vegetable-tanned leather (23.1 cal./g.); the latter had a slightly greater differential heat of wetting. The plots of differential and integral heats of wetting against moisture content are discussed in terms of the mechanism of the absorption of water. The integral heat of wetting of dry hide powder was also measured and the results are compared with those of other workers in this field. J.M.C.

The Nature of Acid Groups Present in Chrome-tanned Collagen and the Pyridine Neutralization Method of Determining Complex-Bound Acid. By P. Hanumanta Rao. *J. Soc. Leather Trades' Chemists*, **39**, 217 (1955). The nature of acid groups which exist in chrome-tanned collagen is discussed. The use of pyridine solution to neutralize the ionic acid groups which are outside the chrome complex is reviewed. A study was made of the diffusion-neutralization method (see K. H. Gustavson, J. Am. Leather Chemists' Assoc., **21**, 559 (1926) and the pyridine neutralization method using hide powder and pelt tanned under various conditions. In one experiment, strips of collagen were tanned for varying periods of time with a sucrose chrome liquor free of organic residues (67 per cent acidity), after which the washed specimens were treated with a 4 per cent pyridine solution for 4 hours, rewashed, and dried. While the Cr_2O_3 content of the tanned strips varied from 3 to 15 per cent the acidity of the chrome complex is shown to be constant between 30 and 35 per cent. The chromium sulfate fixed was of the order of 60-66 per cent acidity and in every case only half of this was removed by the pyridine solution. This indicates that pyridine is able to react with and remove only one of the two apparently chemically distinct types of sulfate present in chrome leather. By reacting the pyridine solution with chrome-tanned hide powder, one-half of which was allowed to dry and the other half kept wet, it is shown that the nature of the protein-bound acid and chrome complex-bound acid does not change on drying the leather. The proportion of unipointly and bi-functionally fixed chromium is calculated from the diffusion neutralization method. Chromium chloride and chromium sulfate in 67 per cent acid solutions are apparently fixed by collagen in the same way probably with 33 per cent acidity of the complex, but the complex in the case of the former is not so stable as in the latter. J.M.C.

The Durability of Leather From Split Hides. By R. F. Innes and R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **39**, 225 (1955). Leather samples were exposed in a gas chamber to which sulfur dioxide was admitted. The deterioration produced was much less

than that found in previous work where the contamination of the atmosphere in the chamber was produced by burning gas containing sulfur compounds. The difference is attributed to the action of sulfur trioxide which, although formed in the flame in relatively small quantities, causes a marked reduction of the exposure period required to initiate deterioration. Owing to the small losses of strength that occurred in the samples exposed in the present study in the gas chamber, the conclusions which were drawn from the experiment were based on measurements of the pH values of water extracts of the exposed pieces. In agreement with the earlier work it is shown that protection is conferred by the presence in the leathers of salts, such as citrates and pyrophosphates. The presence of citrate maintains the water extract pH well above the danger level of 3.0. While both citrate and pyrophosphate hinder the catalytic production of sulfuric acid by ionic iron, pyrophosphate is the more effective. To determine optimum quantities of the two salts that should be added to protect commercial leather requires an experiment of longer exposure time.

J.M.C.

Studies in Chrome Tanning. Neutralization of Chrome Tanned Leather. By Y. Nayudamma and (the late) R. Theis. *J. Soc. Leather Trades Chemists*, **39**, 239 (1955). Accurate knowledge of the acid radicals present in chrome leather is necessary for a proper understanding of the mechanism of the neutralization process employed to remove free acid. Batches of hide powder were tanned in 33-1/3 per cent basic chrome sulfate solutions at their natural pH containing increasing amounts of chromium. The final pH of the tan liquor was recorded and the materials were washed with water adjusted to a pH equal to that of the tanning equilibrium to remove excess chrome liquor. The material was dried with two acetone changes and then air dried. One-gram portions were then neutralized to a desired pH (over a three-day period) by careful addition of NaOH or H_2SO_4. During the neutralization procedure the materials were constantly agitated. The materials were washed with a KCl solution adjusted to the equilibrium pH in each case, after which the washed material was dried in air, ground, and analyzed for total acid sulfate, chrome content, and hide substance. From a plot of total acid sulfate against equilibrium pH the similarity to the acid-base titration curve for native collagen is apparent in the range of pH 1.4 to 4.0. By assuming that up to pH 4.0 only the protein-bound acid is titrated, and deducting the value for acid sulfate at pH 4.0 from that at pH 1.4 a value of 1.08 meq. per g. protein was determined. The close proximity of this value to the acid binding capacity of the hide powder (0.96 meq./g.) before tanning indicates (1) that only the protein-bound acid is being diffused and titrated up to pH 4.0 and (2) the amino groups of the protein may not be involved in the tanning. The chrome complex at pH 4.0-4.5 is quite stable and, at higher pH, OH^- of the alkali penetrates and gradually displaces sulfate to form chromium hydroxide at pH above 6.5-7.0. The basicity of the chrome complex in leather at pH 4.0 is found to be 72 per cent. Based on data obtained, a further modification of Gustavson's method is suggested for determination of protein-bound acid. J.H.C.

The Structure and Deformation of Collagen Fibers. Part I. Plastic and Elastic Deformations Under Pressure. By A. J. Cruise. *J. Soc. Leather Trades' Chemists*, **39**, 252 (1955). The application of pressure to microscopic collagen fibers and fiber bundles gives information regarding the internal structure of the bundles and the effects of various treatments upon the elasticity of the fibers. Use of pressure technique has shown that at least four varieties of collagen structure exist in most skins and that these variants possess different chemical and physical properties. A metal plate carrying a transparent sapphire sphere is substituted for the front lens of a microscope substage condenser. This plate mounted on the optical axis of the system exerts pressure by contact with a coverslip over the specimen. Pressures obtainable are estimated at a maximum of 100,000 kg. per sq. cm.

By determining the width of a collagen bundle before, during, and after compression, an elastic component can be estimated. Qualitative work indicates that separation of fibers under pressure is closely dependent upon their state of hydration and the rate of loss of moisture may govern fiber identity upon drying. Excessive drying temperatures or rates are associated with changes in the array of fibers in the dried bundle, and the surface appearance of the fibers can be emphasized by an interferometer technique. Elasticity is shown to change considerably with method of tanning. The characteristic plasticity of vegetable-tanned fibers may be due to some sort of adhesion between the fibers in the bundles, which is not marked in chrome-tanned fibers. A comparison is made of the effects of pressure on collagen bundles and nylon monofilament by plotting per cent increase in surface area against load. J.M.C.

Health Impairment in Preserving Hides with Sodium Fluosilicate. J. Kerka, F. Pokorny, and F. Picha. *Pracovni Lekarstvi* **7,** 102-4. Through *C.A.*, **49,** 9310 (1955). Cases of acute inflammation of the nasal mucous membrane and acute conjunctivitis are described in workers handling hides in salt contg. 0.1 per cent of Na_2SiF_6. The atm. contained between 0.0014 and 0.0084 mg. Na_2SiF_6 in 1 liter. Hygienic measurements and technological improvements of the manufg. process are suggested.

Paper Chromatographic Determination of Gelatin with Acid Additions. K. Heyns and [illegible]. Walter. *Deut. Lebensm.-Rundschau,* **51,** 65-7. Through *C.A.*, **49,** 9310 (1955). Samples of normal and acidified gelatin (1 g. each) were dissolved in 100cc. H_2O and kept in an incubator for two weeks at 48° or 21 days at 37°. The resulting solns. were dialyzed for 17 hours in 450 cc. distd. H_2O, and the diffusates evapd. under reduced pressure. Each residue was then taken up in 0.4 cc H_2O, subjected to chromatography with a BuOH-AcOH-H_2O mixt., sprayed with ninhydrin soln., and stored for a week in the dark before being evaluated. It was shown that acidified stored gelatin does not decomp. and acts the same as freshly acidified gelatin.

Effect of Ultrasonic Vibrations on Processes of Leather Technology. V. M. Fridman, A. L. Zaides, A. N. Mikhailov, N. N. Dolgopolov, and N. M. Karavaev. *Doklady Akad. Nauk S.S.S.R.,* **92,** 399-400 (1953). Through *C.A.* **49,** 8624 (1955). cf. *C.A.* **48,** 14268a. The effect of ultrasonic vibrations on depilation and tanning was studied with an app. having a frequency of 1200 kc. and a power of 8-10 w. sq. cm. The app. was equipped with a cooling system to maintain const. temp. in the reaction vessel. After 6 hrs. at 30°, the hair and epidermis came off easily and the grain side was smooth; hair and epidermis were not removed in this time by a lime suspension without ultrasonic vibrations. Tanning was complete after 18 hrs. at 30° with, and in 114 hrs. without ultrasonic action. The resulting leather was full, with fibrous microstructure.

The Scalding of Hogskins. A. Kalina. *Kozarstvi* **4,** 46-9 (1954). Through *C.A.* **49,** 7880 (1955). The expts. of Stather (*C.A.* **46,** 7803*bh*) are reviewed. The Dresden method of removing bristles from hogskins by scalding at 59-62° for 4-6 min. is disapproved. About 6 million damaged hogskins show its dangers. Application of H_2O above 55° is dangerous and must not be allowed.

Vegetable Tanning of Prechromed Hides. L. Masner. *Ceskoslov. Kozarstvi,* **3,** 86-7 (1953). Through *C.A.*, **49,** 7881 (1955). Hides for sole leather are pickled at 18-22° in 9-120 per cent H_2O, 6-8 per cent NaCl, 0.8-1.3 per cent H_2SO_4 (100 per cent) for 8-14 hrs. the pickle contains 75-80 g. Na Cl/1. and after pickling, 0.2-0.5 g./1. H_2SO_4. The pH on the surface of hides is 3.6-4.0, in the middle 5.5. To the exhausted pickle a liquor

contg. 0.4-0.8 per cent Cr_2O_3 of 39-42 per cent basicity is added. The tanning lasts 16 hrs. and the pH on the surface of the hide is 4.4-5.0, shrinkage temp. (*Ts*) 76°. For the vegetable tannage in a drum in 120-60 per cent liquor, 24-7 per cent tannin is necessary. For sole leather 20 per cent of the amt. is syntans. The temp. of tanning rises from 26-32° to 40-5° for firm sole leather and to 34-40° for Goodyear welt sole leather. For vegetable-tanned upper leather the hides are pickled in 80-100 per cent liquor 3-6 hrs., with 6-7 per cent NaCl and 0.8-1.0 per cent H_2SO_4. The surface pH of the pickled hides is 3.6-3.8, the middle 4.5-5.0. Chrome tannage in pickle is done with 0.4-0.6 per cent Cr_2O_3, 40-5 per cent basicity, 5-7 Hrs., at 18-20°. The surface and the center of leather have a pH of 4.4-5.0, *Ts* 76°. The vegetable tannage is done in 2 drums with 12 per cent of pure tannin (up to 40 per cent syntans) in 100-180 per cent of liquor. The temp. rises from 20 to 30°. The pH of the tanning liquor (4.2-5.2) is adjusted by Na_2SO_3. In the tanning liquor 2 per cent of sulfonated oil is used. Liquors are changed after 5 packs of hides. It is also possible to pickle hides for upper leather to pH 4.0-4.2 as above, and tan in pickle with 0.5-0.7 per cent Cr_2O_3, basicity of the 40-5 per cent, 5-7 hrs., at 18-20°. The pH of the surface of hides is 4.0-4.5, *Ts* min. 80°. The tannage in the drum follows in 110-40 per cent of liquor at 28-32° 10-12 hrs., with lignin ext. (7-9 per cent pure tannin on pelt) or 11-14 per cent on shaved wt., pH 4.0-4.2. After tannage, the leather is washed with H_2O at 20-5°, for 20-30 min. There follows a second chrome tannage with 80-90 per cent liquor at 18-20, 5-7 Hrs. 3 per cent NaCl and, after 5-8 min., 0.6-0.7 per cent Cr_2O_3 of 40-5 per cent basicity are given. The pH of the leather, 4.0-4.2, is adjusted by means of Na_2CO_3. After the second tannage the leather is washed 30-60 min. H_2O at 20-2°. The fatliquoring of firm sole leather is adjusted to give 2-3 percent fat, for Goodyear welt sole leather 3.5-4.5 per cent, for upper leather 20-2 per cent. For the filling of sole leather 1.5-2.0 per cent $MgSO_4 \cdot 7H_2O$ and 5 per cent glucose are used.

Short Liming for Glazed Kid. V. Nespor. *Ceskoslov. Kozarstvi*, **3**, 59-61 (1953). Through *C.A.*, **49**, 7881 (1955). Short and long liming of glazed kid were investigated. Short liming is especially advantageous for smaller skins of av. (dry) wt. of 300 g. (2-3 foot leather). With long liming, the output of leather of 0.1-0.25 mm. thickness was 5-10 per cent from this wt. class. Leather from short liming is considerably fuller, less veiny, with smaller flank. The grain is somewhat pronounced, which is an advantage for these small skins. The pressure of glazing should be reduced. The short liming is advantageous also for larger skins. (4.5-5.5 ft.). The painted skins should not be piled, but rather suspended up on poles. The penetration of paint is more uniform and the hair is better.

Relation between the Shake and Filter Bell Methods of Tannin Analysis. A. Stehlik, M. Goisova, and B. Lacnakova. *Kozarstvi*, **4**, 105-7 (1954). Through *C.A.* **49**, 7883 (1955). The results can be calcd. according to the equation $T=T_1+N_1(1-N/N_1)$, in which T=tannin by the filter bell (*I*) method of analysis, N nontannins by *I*, T=tannin by the shake method (*II*), and N_1= nontannins by (II). The value N/N_1, characteristic for each tanning material, must be known and be const. These values have been detd. by the Czechoslovakian standard hide powder. Values $K=1-N/N_1$ *and* $K_1=N_1/N$ have been detd. For quebracho ordinary, quebracho-fulfited, Syntan K_2D, Syntan SN_{25}, Kortan QU 1, Svitanid (lignin ext.), spruce, chestnut, oakwood exts., and valonia K_1 is 0.7, 0.44, 1.62, 1.43, 0.59, 0.09, 0.20, 0.30, 0.34, and 0.41, resp. K_1 is 0.41, 0.31, 0.62, 0.59, 0.37, 0.08, 0.17, 0.23, 0.25, and 0.29, resp. A table of results is given. N_1/N varies for spruce ext. from 1.13 to 1.23, for syntan K_2D from 1.95 to 3.30, for sulfited quebracho from 1.38 to 1.48. These values are less const. for syntans than for natural tannins.

Driers for Pasted Leather. B. Plechac. *Kozarstvi*, **4,** 104-5 (1954) Through *C.A.*, **49,** 7884 (1955). Defects of driers and of drying are discussed. Special glass plates with low internal stresses are necessary. Bad pasting is generally caused by too wet leather (over 65 per cent H_2O), by dry edges of leather, or by a bad paste. Leathers dried at the same time should be as uniform in thickness and area as possible.

Paste-Drying of Leather. B. Plechac. *Kozarstvi*, **4,** 65-70 (1954). Through *C.A.* **49,** 7884 (1955). The flow of air in driers is discussed. A slowly circulating, air-conditioned air current saves heat. A forced air-draught is necessary. The up-down direction of air flow is recommended. The down-up system gives slower drying. The poor holding of leather on glass plates is due to wrong technology of pasting. The head of the side ought to be upward; this gives a more uniform distribution of tension during the drying. The H_2O content of chome- and vegetable-tanned leathers was ascertained at different relative humidities of the atm. Cr-leather gains and loses H_2O more quickly. The hysteresis of both leathers is about the same. A diagram of a 6-independent section pasting drier is given. The leather must be wrung to 55-60 per cent H_2O content before pasting.

New Methods for the Finishing of Leather. V. Pektor. *Ceskoslov. Kozarstvi*, **3,** 165-6, 177-80 (1953). Through *C.A.*, **49,** 7884 (1955). A review of current practice of pasting leather, applying resin dispersions, and infrared drying of finishes on side upper leather. Energy consumption data are given for infrared drying. The most advantageous wave lengths are 10,000-13,000 *A*.

Higher Quality of Sole Leather. A. Kala. *Ceskoslov. Kozarstvi*, **3,** 154-6, 181 (1953). Through *C.A.*, **49,** 7885 (1955). The physicomech. evaluation of sole leather is more important than the chem. A higher content of syntans usually raises the H_2O-absorption value and abrasivity. The hydrothermic stability (**I**) (loss of tensile strength after 24 hrs. at 50 and 100 per cent relative humidity) can be raised by chrome pretannage. K. has followed these properties on different types of tannage and methods of loading sole leather. **I** of normal sole leather is 15.4-22.2 per cent. In the same leather loaded with H_2O-sol. urea-HCHO condensation products, softened by coumarone resins, **I** is 87.0-93.4 per cent. In chrome-pretanned leather **I** is 86.0 per cent; The H_2O absorption of these leathers is 39.1-45.5, 36.4-39.7, and 49.0 per cent resp. Resistance to abrasion (Stather and Herfeld, *C.A.* **33,** 3627[8]) is 2790, 7540, and 6810 resp.

Problems of Chemical Analysis of Leather. V. Kubelka, Jr., and A. Blasej. *Kozarstvi*, **4,** 230-4 (1954). Through *C.A.*, **49,** 7885 (1955). The detn. of leather substances is of most interest. The detn. of H_2O gives low results on leathers high in fats, which gain wt. on oxidation. Ash should be calcd. on hide substance, otherwise the conclusions may be false. Since inorg. compds. volatilize (NH_4 salts at 300-500, chlorides over 600), conversion to sulfate is perhaps best. The sulfated ash is 10-20 per cent higher than the original ash. By detg. fat with CCl_4 or petr. ether only true fats are obtained; oxidized fats must be extd. by Et_2O, hydroxy acids by a 1:1 mixt. of EtOH and $CHCl_3$, bound fats after hydrolysis with 15 per cent KOH, acidification with 15 per cent H_2SO_4, and extn. with petr. ether. Glycerol is insol. in org. solvents. The pH of the aq. ext. does not det. acid already bound on leather after long storage. The detn. of N in leather may be influenced by the presence of N-contg. syntans, but not of NH_4 salts. The calcn. of leather substance according to Kubelka (*C.A.* **31,** 8243[8]) is wrong for chrome-retan leathers. The authors propose, therefore, to calc. the leather analysis on hide substance. In the calcn. of leather substance of chrome leather, 1 per cent Cr_2O_3 is equiv. to 2.87 per cent Cr-tanning material in leather (Kubelka, *C.A.* **47,** 9651i). Examples are given.

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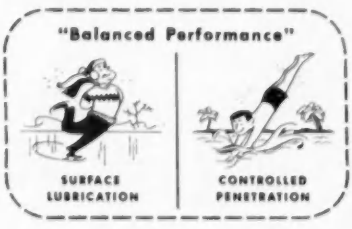

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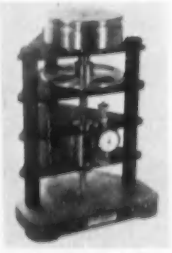

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CS-7ILL	1 lb.	30	.0005"	.030"
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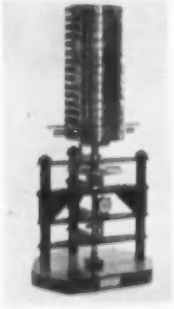

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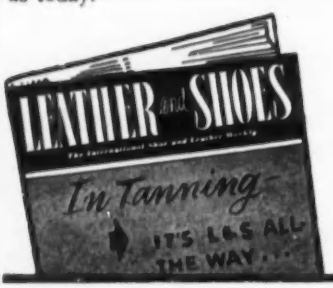

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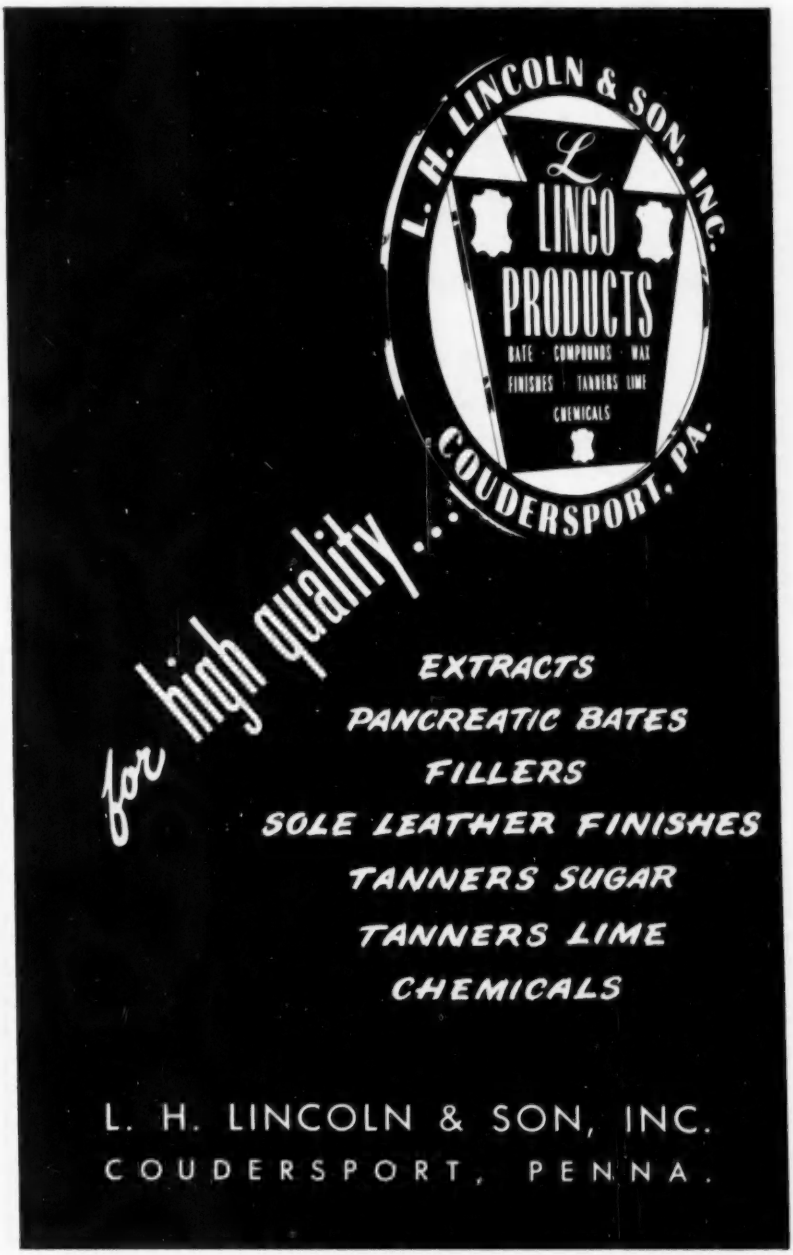
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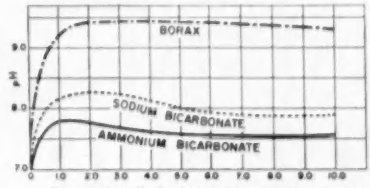

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